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AN INVESTIGATION OF THE EFFECT OF SURFACE IMPURITIES
ON THE ADSORPTION KINETICS OF HYDROGEN CHEMISORBED ONTO IRON

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1.0 INTRODUCTION

The goal of this program has been to develop an understanding of heterogeneous kinetic processes for those molecular species which produce gaseous hydrogen degradation of the mechanical properties of metallic structural materials. Although hydrogen degradation of metallic materials is believed to result from dissolved protonic hydrogen [1,2], the heterogeneous hydrogen interface transport processes often dominate the kinetics of degradation [3]. The initial step in the interface transport process is the dissociative chemisorption of the molecular species at the metal surface followed by hydrogen absorption into and transport through the bulk [4].

Modern advanced aerospace applications often require the use of structural materials in high pressure hydrogen environments at temperatures which range from low cryogenic temperatures to very high temperatures (1300 K and greater) [5]. Materials proposed for these applications, such as the titanium aluminides, beta-titanium alloys, iron-, nickel- and cobalt-based superalloys, and molybdenum-rhenium alloys need to possess a high degree of immunity from hydrogen induced degradation of mechanical properties. Little is known about the interaction of hydrogen with many of these materials and the possible influence of hydrogen on the material's mechanical properties [6]. It can be expected that the interaction of gaseous environmental hydrogen with these materials will be influenced by the gas phase-surface reaction process as well as the bulk transport process [7]. The present study was established in 1988 to develop an understanding of the interaction of gaseous hydrogen with these materials and to evaluate hydrogen transport through them. This study supersedes, for the present, the work begun earlier under this agreement, which was to study the influence that surface impurities have in modifying the kinetics for hydrogen chemisorption on pure iron.

During the present program, the interaction of hydrogen with the surfaces of alpha-2 (Ti_3Al) titanium aluminide [8], gamma (TiAl) titanium aluminide [9], and beryllium [10] were studied. The interaction of low pressure hydrogen with gamma titanium aluminide and beryllium was found to be relatively weak. Weak in the sense that adsorption leads to a low surface concentration of dissociated hydrogen, i.e., the chemisorption process is reversible at room temperature (300 K) for gamma titanium aluminide and the sticking coefficient for chemisorption is extremely small for beryllium. Hydrogen was found to interact readily with alpha-2 titanium aluminide to form a stable surface hydride at 300 K. These results correlate well with other recent studies which show that the mechanical properties for alpha-2 titanium aluminide are readily degraded in hydrogen while gamma titanium aluminide exhibits less degradation and beryllium essentially no degradation [11]. The interaction of oxygen with the surface of several of these materials was studied, also [12]. More recently, preliminary hydrogen permeation studies were completed for three high temperature alloys, Incoloy 909 [13], Mo-47.5Re (wt.%) [14], and this past year, Haynes 188 [15].

The remainder of this document presents a narrative summary of the research activities completed during the award period, January 1, 1994 to December 31, 1994.

2.0 SUMMARY OF RESEARCH ACTIVITIES

Work supported by this agreement has covered a spectrum of activities during the present award period. The focus of the technical activity was to complete the initial study of hydrogen and deuterium permeation in Haynes 188 alloy. A portion of time was spent on non-research activities in providing technical support to the National Aeronautics and Space Administration (NASA). In this regard, a small surface analysis study was undertaken to characterize the oxide surface formed on a nickel alloy during a specific brazing procedure. There was concern, also, about the loss of alloy constituents as a result of the process. The study helped establish the optimum brazing procedures and demonstrated that alloy constituents were not being lost during the procedure. In addition, time was spent in completing a critical review of the existing database of randomly performed measurements of hydrogen absorption in the titanium aluminide alloy Ti-24Al-11Nb. From this study, a technical report was prepared describing the most plausible parameters for hydrogen solubility in this alloy. From the technical report a publication manuscript was prepared, a copy of which is attached as Appendix I.

2.1 Permeation - Experimental

The high temperature measurements of H_2 and D_2 permeation through a 0.020 in thick Haynes 188 alloy specimen were completed. These measurements were conducted over a temperature range of 250 to 880 C and a pressure range from $1.3 \times 10^3 \text{ N/m}^2$ to about $1.2 \times 10^5 \text{ N/m}^2$. The results from the H_2 measurements have been analyzed and are described in detail in ref. 15. Since ref. 15 has not yet been published, a copy of the publication manuscript is attached as Appendix II. The data from the D_2 measurement have not been analyzed at this time.

2.2 Permeation - Modeling

There were no significant research activities in the permeation modeling area during the present award period.

2.3 Surface Characterization

There were no significant research activities in the surface characterization area during the present award period.

2.4 Other Activities

A. Meetings Attended (present award period)

1. Fifth International Conference on Hydrogen Effects on Material Behavior, September 11-15, 1994, Jackson Lake Lodge, Wyoming, presenter and participant.

B. Presentations Made (present award period)

1. Hydrogen Solubility in Ti-24Al-11Nb, contributed presentation, Fifth International Conference on Hydrogen Effects on Material Behavior, Jackson Lake Lodge, Wyoming, September 11-15, 1994.
2. Comparison of Lattice Hydrogen Transport Parameters for the High Temperature Alloys, Incoloy 909, Haynes 188, and Mo-47.5Re, Fifth International Conference on Hydrogen Effects on Material Behavior, Jackson Lake Lodge, Wyoming, September 11-15, 1994.

C. Publications

The following have been published, submitted for publication, or were in preparation for publication during the present award period:

1. Diffusivity and Solubility of Deuterium in a Mo-Re Alloy, *Scripta Metallurgica et Materialia*, 30(1994)749.
2. Hydrogen (D₂) Permeation in INCO 909 and Mo-Re Alloys: Preliminary Results, in *Summary Proceedings of the 5th Workshop on Hydrogen-Material Interactions*, NASP Workshop Publication 1014, H.G. Nelson, ed. (NASA-Ames Research Center, April, 1994) p. 379.
3. A Study of the Interaction of Hydrogen with the Surface of Titanium-Aluminum Intermetallic Alloys, in *Proceedings of the Third International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications*, (Uppsala, Sweden, 1992), D. Noréus, S. Rundqvist, and E. Wicke, eds. (R. Oldenbourg Verlag, München, 1994) p. 1016.
4. Hydrogen Solubility in Ti-24Al-11Nb (with S.N. Sankaran and A.W. Thompson), to be published in the *Proceedings of the Fifth International Conference on Hydrogen Effects on Material Behavior*, Jackson Lake Lodge, Wyoming, September 11-15, 1994.
5. Comparison of Lattice Hydrogen Transport Parameters for the High Temperature Alloys, Incoloy 909, Haynes 188, and Mo-47.5Re, to be published in the *Proceedings of the Fifth International Conference on Hydrogen Effects on Material Behavior*, Jackson Lake Lodge, Wyoming, September 11-15, 1994.
6. ESR Studies of Dilute Local Moment Alloys, Harris Flam, Mickey R. Shanabarger, and S. Schultz, in preparation.

D. Technical Reports

1. An Investigation of the Effect of Surface Impurities on the Adsorption Kinetics of Hydrogen Chemisorbed onto Iron, M.R. Shanabarger, Annual Status Report, NASA-Ames Cooperative Agreement No. NCC-2-63, January 1 to December 31, 1992, submitted to Howard G. Nelson, NASA-Ames Research Center, February, 1994.
2. Hydrogen Solubility in Ti-24Al-11Nb (at.%), final version, submitted to H.G. Nelson of NASA-Ames Research Center, February, 1994.

3.0 REFERENCES

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2. M.R. Shanabarger, in *Second Workshop on Hydrogen Effects on Materials in Propulsion Systems*, B.N. Bhat, D.L. Dreshfield, and E.J. Vesely, Jr., eds., NASA Conference Publication 3182(1992), p.12.
3. H. G. Nelson, D. P. Williams, and A. S. Tetelman, *Metall. Trans.* 2(1971)953.
4. *Chemisorption of Gases on Metals*, F.C. Tompkins (Academic Press, New York, 1978).
5. Advanced Materials to Fly High in NASP, T. M. F. Ronald, *Advanced Materials and Processes* 135(May, 1989)29.
6. *Summary Proceedings of the Workshop on Hydrogen-Material Interactions*, NASP Workshop Publication 1001, H.G. Nelson and M.R. Shanabarger, eds., (NASP Joint Program Office, Wright-Patterson AFB, Ohio, 1987).
7. M. R. Shanabarger, in *Second Workshop on Hydrogen Effects on Materials in Propulsion Systems*, B.N. Bhat, R.L. Dreshfield, and E.J. Vesely, Jr., eds., NASA Conference Publication 3182, 1992, p.12.

8. M.R. Shanabarger, in *Hydrogen Effects on Material Behavior*, N.R. Moody and A.W. Thompson, eds. (The Minerals, Metals & Materials Society, Warrendale, 1990), p.507.
9. M.R. Shanabarger, in *Summary Proceedings of the Third Workshop on Hydrogen-Material Interactions*, NASP Workshop Publication 1007, H.G. Nelson, ed. (NASP Joint Program Office, Wright-Patterson AFB, Ohio, 1990) p.205.
10. An Investigation of Hydrogen Adsorption on Beryllium, M.R. Shanabarger, to be published in the *Proceedings of the Fourth NASP Workshop: Hydrogen-Material Interactions*, Scottsdale, Arizona, 1990.
11. See articles in *Proceedings of the Fourth NASP Workshop: Hydrogen-Material Interactions*, Scottsdale, Arizona, 1990, to be published.
12. M.R. Shanabarger, *Materials Science and Engineering*, A153(1992)608.
13. M.R. Shanabarger, *Scripta Metallurgica et Materialia*, 8(1993)1143.
14. M.R. Shanabarger, *Scripta Metallurgica et Materialia*, 30(1994)749.
15. M.R. Shanabarger, to be published in the *Proceedings of the Fifth International Conference on Hydrogen Effects on Material Behavior*, Jackson Lake Lodge, Wyoming, 11-15 September, 1994, A.W. Thompson and N.L. Moody, eds.

APPENDIX I

Hydrogen Solubility in Ti-24Al-11Nb

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Proceedings of the Fifth International Conference on Hydrogen Effects on Material Behavior

Jackson Lake Lodge, September 11-15, 1994

HYDROGEN SOLUBILITY IN Ti-24Al-11Nb

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Abstract

Recent reports on measurements of gas phase hydrogen solubility in the titanium aluminide alloy, Ti-24Al-11Nb (at.%), do not give a consistent picture for the solubility of hydrogen in this alloy [1,2]. The data and procedures employed in these two reports as well as a variety of limited-scope, published journal reports and unpublished government sponsored research reports were reviewed. The compiled data lead to a consistent result for the high temperature, low pressure hydrogen solubility. No compelling evidence is found for hydride formation in this alloy for total hydrogen concentrations less than about 13 at.%.

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Introduction

Two recently published studies of hydrogen absorption in the two phase, alpha-2 titanium aluminide alloy, Ti-24Al-11Nb (at.%) have described significantly different results for the solubility of hydrogen in this alloy. In the study published by Chu, Thompson, and Williams (CTW) [1], the hydrogen solubility as a function of temperature and equilibrium hydrogen pressure was determined by a combination of techniques which included measuring the weight gained by the specimen due to hydrogen absorption. The most recent study published by Sankaran, Herrmann, Outlaw, and Clark (SHOC) [2], used gas phase permeation techniques to estimate the hydrogen solubility from the measured temperature and pressure dependence of the hydrogen permeability and diffusivity. The results from these two studies contain significant differences in the amount of hydrogen absorbed under identical low pressure hydrogen charging conditions, differences in the heat of solution, and in the observation of hydride phases.

In an attempt to resolve these differences and possibly understand their origin, additional sources of data for hydrogen adsorption in this and similar alloys have been reviewed. Some of these data exist in the accessible published literature, while other data are scattered in various reports of government sponsored program research on this and related subjects. The majority of these reports contain limited data, since most of the studies were preliminary in nature. The one exception is the published study of hydrogen absorption in the binary alpha-2 titanium aluminide alloy, Ti₃Al, from which the ternary alloy Ti-24Al-11Nb is derived [3]. This study provides a good basis for comparison with the other works.

This review was initiated at the request of the National Aeronautics and Space Administration and involved the collaborative effort of the principle investigators for the work reported in ref. 1 (A. W. Thompson) and ref. 2 (S. N. Sankaran).

Review of Available Data

All sources of data relevant to this issue and known to the authors were reviewed and are summarized below. Many of these studies are limited in scope and provide only a few data points. All described experimental methodologies and analyses were reviewed with corrections to the analyses noted where appropriate. The *total hydrogen uptake* is defined to be the total measured (or interpolated) equilibrium hydrogen content at a given temperature and pressure. For this review, the total hydrogen uptake is quoted for the fixed pressure of 133 N/m² (1 torr). The *hydrogen solubility* is defined as the slope of the total hydrogen uptake as a function of the square root of the pressure evaluated at low pressures and for fixed temperatures. The hydrogen solubility determines the lattice hydrogen concentration, whereas the total hydrogen uptake may contain an additional contribution due to hydride formation. The total hydrogen uptake data is summarized in Table I and Fig. 1 and the hydrogen solubility data is summarized in Table II and Figure 2.

Government Sponsored Program Research

1. Analytical Services and Materials, Inc. (ASM)

Isothermal measurements of hydrogen uptake and solubility in Ti-24Al-11Nb alloy were made over the temperature range 500 to 800 C and for pressures up to about 4×10^4 N/m² (300 torr) [4-6]. The specimens were fabricated from a commercially prepared rolled plate. Hydrogen uptake was determined by specimen weight gain in an ultra high vacuum thermogravimetric apparatus. Except for the data at 500 C, the hydrogen uptake obeys Sievert's Law over the measured pressure range. The data for 500 C display a deviation from Sievert's Law at higher

pressures. The nature of the deviation is suggestive of limited-site, single phase absorption and not hydride formation. No microstructural or X-ray diffraction evidence of hydride formation was found after hydrogen charging. In fact, the initial microstructure seemed quite stable in the presence of hydrogen for these charging conditions. These data were acquired from repeated measurements conducted over an extended period of time. It should be noted that these data were acquired independently from the permeability derived solubility data obtained by the same organization and published in ref. 2 [7].

TABLE I: Hydrogen Uptake (at.% H) at 133 N/m^2 (1 torr).

Temperature (°C)	ASM (24-11)	Grumman (24-11)	P&W (super α_2)	CTW* (24-11)	RRW (Ti ₃ Al)
800	0.39				
760			0.59		
			0.68		
750					0.74
700	1.11	0.74			
	0.73				
650	1.87			5.1	1.40
600	1.56			5.9	
550	3.03			6.8	2.86
500	4.07			9.4	
	4.36				

* These values are taken from Fig. 5 of ref. 1.

2. Grumman Aerospace Corporation (Grumman)

In this work, isothermal uptake data were acquired at 700 and 900 C for pressures up to $1 \times 10^5 \text{ N/m}^2$ (760 torr) [8]. The specimens were charged in a Sievert's apparatus. After charging, the apparatus was quenched to room temperature and the amount of hydrogen absorbed by each specimen confirmed with independent vacuum hot extraction measurements. The Ti-24Al-11Nb alloy was obtained as commercially produced rolled plate. The initial microstructure was predominantly equiaxed α_2 phase with about 8% discontinuous β phase. The absorption data taken at 700 C obeyed Sievert's Law over the indicated pressure range; corresponding data taken at 900 C show deviations from Sievert's Law for pressures above $4.8 \times 10^4 \text{ N/m}^2$ (360 torr). Microstructural analysis of the charged specimens had not been completed at the time the uptake data was reported. A complete and detailed discussion of this work is in preparation [9].

3. Pratt & Whitney Engineering Division (P&W)

Isothermal measurements of hydrogen absorption in a commercial super alpha-2 titanium aluminide alloy (Ti-25.8Al-11.2Nb-3.3V-0.25Mo, at.%) were made at 760 C over the pressure range $1.3 \times 10^2 \text{ N/m}^2$ to $1.3 \times 10^5 \text{ N/m}^2$ (1 to 1000 torr) [10]. Although super alpha-2 has a slightly different composition compared with the alloy of interest, the data is still expected to be relevant to the present discussion. No microstructure studies were reported for the starting material nor for the charged specimens. Also, no details of the charging procedure were provided. Hydrogen uptake was determined from specimen weight gain. From the data presented in ref. 10, it was possible to obtain estimates of the total uptake as well as the solubility. The data accurately obeyed Sievert's Law over the indicated pressure range.

TABLE II: Hydrogen Solubility, at.% H/(N/m²)^{1/2}

Temperature (°C)	ASM (24-11)	Grumman (24-11)	P&W (super α_2)	CTW* (24-11)	RRW (Ti ₃ Al)	GE (24-11)
1050						0.018
900		0.030				
800	0.025					
760			0.041			
750					0.064	
700	0.060	0.064				
650	0.160			0.448	0.124	
600	0.151			0.520		
	0.110					
550				0.678	0.256	
500	0.361			0.850		
	0.331					

* Values calculated from data presented in Fig. 3 of ref. 1.

Published Work

4. Chu, Thompson and Williams (CTW)

Isothermal measurements were made with a commercially obtained Ti-24Al-11Nb alloy over the temperature range of 350 to 725 C and the pressure range of 1.3×10^{-1} N/m² to 1×10^5 N/m² (10^{-2} to 760 torr) [1]. This particular work presently represents the most complete published study of hydrogen absorption in this particular alloy. After solution treating, the alloy was aged at 705 C for 120 minutes and air cooled. The microstructure was essentially 100 % α_2 phase. The absorption measurements were conducted in a Sievert's apparatus and hydrogen uptake was determined primarily from specimen weight gain. Full reversibility was confirmed several different ways. The appearance of a second phase is observed in the uptake data. This is assumed to be a hydride phase observed visually with metallography techniques and by X-ray diffraction in specimens with hydrogen concentrations greater than 13 at. %.

5. Rudman, Reilly and Wiswall (RRW)

This appears to be the first reported work on hydrogen absorption in an intermetallic titanium aluminide [3]. The study was done over the temperature range of 450 to 800 C and at pressures up to 1.3×10^4 N/m² (100 torr) with homogenized, single phase specimens of Ti₃Al (Ti-24.8Al at.%, measured composition). Melted buttons of the alloy were annealed at 1000 C before being ground into powders. All the absorption measurements were done on powders. The isothermal hydrogen uptake was determined by changes in hydrogen pressure in the reaction vessel. Isotherms were confirmed to be reversible, at least for temperatures above 500 C. Data below 500 C were considered suspect by the authors. The absorption isotherms were not consistent with hydride formation. They were consistent, however, with site-limited single phase absorption. A phase determination on the charged powders was not performed.

6. Sankaran, Hermann, Outlaw, and Clark (SHOC)

Gas phase permeation techniques were employed to measure the permeability and diffusivity of hydrogen in a Ti-24Al-11Nb alloy [2]. These measurements were made over the temperature range of 500 to 900 C and the pressure range of 20 to 1.3×10^3 N/m² (0.15 to 10 torr). The hydrogen solubility was estimated from the measured pressure and temperature dependence of the permeability and diffusivity. The permeation membranes were machined from rolled plate and vacuum annealed at 1100 C for 90 minutes. The initial microstructure

consisted of equiaxed alpha-2 grains with small amounts of beta-phase at the grain boundaries and an orthorhombic phase at the triple points. After hydrogen exposure the microstructure consisted of an alpha-2 matrix with a discontinuous beta phase at the grain boundaries. The membranes showed no evidence of a hydride phase. The hydrogen solubility determined in this work is given by $1.7 \times 10^{-4} \exp (41.2 \text{ kJ/mole}/RT) \text{ at.}\% \text{ H}/(\text{N/m}^2)^{1/2}$ and is shown as the dashed line in Fig. 2.

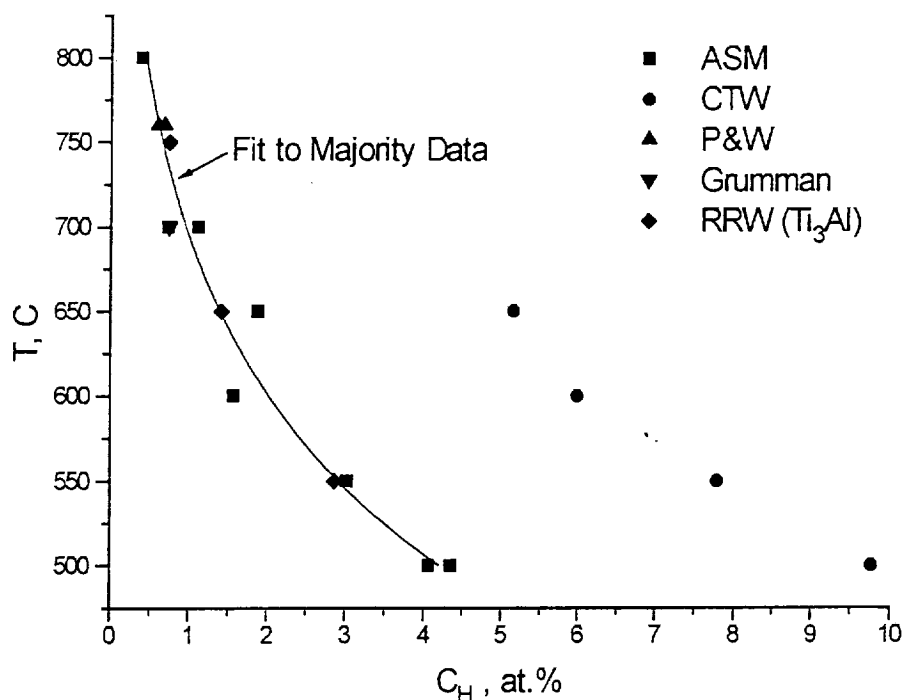


Figure 1. Total hydrogen uptake in nominal Ti-24Al-11Nb (at.%) alloys at 133 N/m^2 (1 torr.)

7. Shih, Scarr and Wasielewski (SSW)

Essentially all of the absorption measurements reported in this particular study are not useful for our purposes, since the specimens were cooled to room temperature in hydrogen from the charging temperature and do not represent the hydrogen concentration in the alloy at temperature [11]. The one exception to this procedure was a measurement for Ti-24Al-11Nb that was obtained by quenching the specimen in an oil bath. This single datum at a charging pressure of $1 \times 10^5 \text{ N/m}^2$ (760 torr) was used to estimate the hydrogen solubility at 1050 C, assuming that Sievert's Law was obeyed. The alloy specimens were initially vacuum annealed at 900 C for 90 minutes and furnace cooled prior to the absorption studies. Microstructural analysis indicated that the starting material was 90 % alpha-2 phase and 10 % beta phase. Hydrogen uptake was determined by specimen weight gain. Although hydrides were observed for hydrogen concentrations greater than 13 at.% H, there is no mention of hydride formation in this lower concentration (6 at.% H), oil-quenched specimen.

Discussion

Presented in Fig. 1 is a plot of the isobaric data presented in Table I for the hydrogen uptake at a constant pressure of 133 N/m^2 (1 torr). The solid line shown in the figure is a least squares fit to the ASM, Grumman, and P&W data. Note that the data for Ti_3Al (RRW) is essentially

indistinguishable from the least-squares fit. The difference between the majority of the data, represented by **ASM**, **Grumman**, **P&W**, and **RRW**, and the **CTW** data is very apparent [12]. Although not presented here, the hydrogen uptake reported in the **CTW** study actually exceeds the corresponding uptake reported for alpha titanium [13]. The **CTW** study reported, also, the presence of hydrides for the concentrations of hydrogen shown in Fig. 1, whereas hydrides were not observed (or reported) in the other studies for similar charging conditions. Subsequent work has determined that the phase reported as hydride by **CTW** is in fact the orthorhombic phase [14].

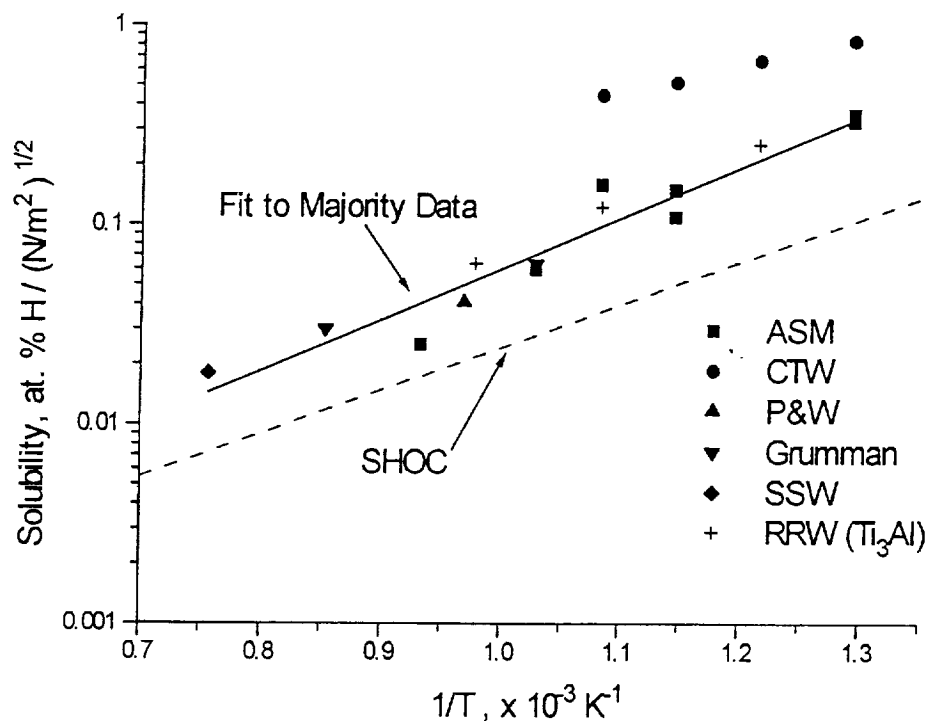


Figure 2. Temperature dependence of the hydrogen solubility for Ti-24Al-11Nb (at.%).

The hydrogen solubility data from Table II is summarized as an Arrhenius plot in Fig. 2. A least squares fit to the majority data (excluding the **SHOC** and **CTW** data) is shown by the solid line which is described by the equation, $1.7 \times 10^{-4} \exp(48.8 \text{ kJ/mole}/RT)$ at.% $H/(N/m^2)^{1/2}$. As can be seen from Fig. 2, the **SHOC** data *underestimates* the majority result by about a factor of two over the indicated temperature range, whereas the **CTW** data *overestimates* the majority result, also, by a factor of about two [15]. At high temperature, extrapolations of the **SHOC** data and the majority data approach each other, since they have the same solubility prefactors (1.7×10^{-4} at.% $H/(N/m^2)^{1/2}$). At lower temperatures, the solubilities diverge because of differences in the estimated heat of solution, -41.2 kJ/mole for the **SHOC** data and -48.8 kJ/mole for the majority data. The heat of solution obtained from the limited **CTW** data set is about -26 kJ/mole, significantly different from either the **SHOC** or majority results. For reference purposes, the corresponding value for alpha titanium is -47.7 kJ/mole and -55.6 kJ/mole for beta titanium [3].

The studies on nominal Ti-24Al-11Nb alloys (including Ti_3Al) are in agreement with the expectations of limited-site, single phase absorption. The data for super alpha-2 (Ti-25.8Al-11.2Nb-3.3V-0.25Mo, at.%), show no deviation from Sievert's Law up to the maximum

pressure employed in that study, $1.3 \times 10^5 \text{ N/m}^2$ (1000 torr) [10]. Except for the conclusion expressed in **CTW**, which is probably in error, there is general agreement that hydrides are not present, at least for hydrogen concentrations below about 13 at.%, the typical maximum hydrogen solubility limit achieved in the various studies.

Conclusions

Based on this review of all known available data, we conclude that the hydrogen solubility for Ti-24Al-11Nb can be described by, $S = 1.7 \times 10^{-4} \exp(48.8 \text{ kJ/mole}/RT)$, at.%H/(N/m²)^{1/2} over the temperature range of 500 to 1000 C and pressures up to $1.3 \times 10^5 \text{ N/m}^2$ (1000 torr). For the indicated temperature and pressure ranges, there is no evidence of hydride formation. The conclusions presented by **CTW** [1] are at variance with the above conclusions, whereas the **SHOC** study [2] shows mild disagreement. The origin of these differences were not speculated upon in this report.

References and Footnotes

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4. S.N. Sankaran, private communication to H.G. Nelson, NASA-Ames Research Center, May 20, 1993.
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7. Complete results of the thermogravimetric study will be published elsewhere.
8. Grumman Corporate Research Center, "Progress Report for January-September 1992. Study of Hydrogen Solubility, Distribution and Precipitation in Titanium Aluminides, NASA Contract NAS2-13183" (submitted to H.G. Nelson, NASA-Ames Research Center, October 16, 1992).
9. Final report in preparation for publication as a NASP Contractor Report.
10. Pratt & Whitney Engineering Division, "Effects of Hydrogen on Titanium Aluminides and Beryllium Materials, Final Report, 9 May 1988-9 February 1991, NASA Contract NAS1-18612" (NASP Contractor Report 1121, August 1991).
11. D.S. Shih, G.K. Scarr and G.E. Wasielewski, Scripta metall., 23(1989), 973.
12. The **CTW** data used in Fig. 1 (this work) was obtained from Fig. 5 of ref. 1. It was assumed in the present work that the pressure values listed in the figure caption for Fig. 5 are the correct values, since they do not agree with the values attached to the curves in the figure.
13. A.D. McQuillan, Proc. Royal Soc.(London), 204A(1950), 309.
14. X. Pierron and A.W. Thompson, "Hydrogen Effects on Mechanical Behavior in the Alloy Ti-25Al-10Nb-3V-1Mo," in Fatigue and Fracture of Ordered Intermetallic Materials, ed. W.O. Soboyejo, T.S. Srivatsan and D.L. Davidson (Warrendale, PA: The Metallurgical Society, 1994), 355-368.
15. It is noted that **CTW** provide a summary equation to describe the hydrogen solubility for Ti-24Al-11Nb, eq. 6 of ref. 1. This equation can be made to reasonably fit the majority fit of the present work over the limited **CTW** temperature range by *redefining* the *pressure units* of eq. 6 (ref. 1) from *Pa (N/m²)* to *0.1MPa (1 x 10⁵ N/m²)*. The predicted solubilities are not, however, internally consistent with the data that is presented in **CTW**.

APPENDIX II

Comparison of Lattice Hydrogen Parameters for the High Temperature Alloys, Incoloy 909, Haynes 188, and Mo-47.5Re

to be published in
Proceedings of the Fifth International Conference on Hydrogen Effects on Material Behavior
Jackson Lake Lodge, September 11-15, 1994

**COMPARISON OF THE HIGH TEMPERATURE HYDROGEN TRANSPORT
PARAMETERS FOR THE ALLOYS, INCOLOY 909, HAYNES 188, and Mo-47.5Re**

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Abstract

Employing a basic, gas phase-permeation measurement procedure and modern, ultra-high vacuum technology, measurements were made of the hydrogen permeability and diffusivity in Incoloy 909, Haynes 188, and Mo-47.5Re (wt.%). For reasons of measurement sensitivity, deuterium was substituted for hydrogen in the Mo-47.5Re measurements. The hydrogen (deuterium) solubility for each alloy was estimated from the relationship between the permeability and diffusivity. The transport parameters obtained from these measurements are compared against each other. These parameters were determined over a typical pressure range of $0.013 - 1 \times 10^5 \text{ N/m}^2$ (10 to 800 torr) and temperature range, 260 to 816 C (500 to 1500 F).

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Introduction

The realization of advanced aerospace propulsion systems is contingent upon the development of structural materials capable of successfully containing high temperature, high pressure hydrogen environments [1]. Three potential candidates for this task are the superalloys Incoloy 909 [2] and Haynes 188 [3], and the refractory metal alloy, Mo-47.5Re (wt.%). Incoloy 909 is a Fe-Ni-Co based alloy while Haynes 188 is a Co-Cr-Ni-W based alloy. The nominal composition of each of these alloys is shown in Table I. Except for Incoloy 909, which is very similar in composition to Incoloy 903, little was known of the hydrogen transport parameters (i.e. permeability, diffusivity, and solubility) for these alloys. Knowledge of these parameters is important not only for propulsion system design, but also for design and interpretation of the mechanical tests required to properly evaluate the effect of the hydrogen environment on the mechanical properties of the alloys [4].

Table I. Nominal Alloy Composition (major components) in Atomic %.

	Co	Ni	Fe	Cr	W	Nb	Mn	Ti	Mo	Re
Incoloy 909	13	38	44			2.9		1.8		
Haynes 188	40.4	22.3	3.4	26.4	4.8		1.4			
Mo-47.5Re									68.2	31.8

In this report, a comparison is made of the transport parameters for Incoloy 909, Haynes 188, and Mo-47.5Re. A determination of the hydrogen transport parameters for Incoloy 909 and Mo-47.5Re have been reported recently [5,6]. The parameters for Haynes 188 are reported here for the first time. The transport parameters in these studies were obtained from gas phase permeation measurements. The measurements covered a pressure range from 1.3×10^3 N/m² to 1.0×10^5 N/m² (10 to 800 torr) and a temperature range of 260 to 816 C (500 to 1500 F).

The data show that the hydrogen permeability and solubility values for Mo-47.5Re are at least two orders of magnitude smaller than comparable values for Incoloy 909 and Haynes 188 for the indicated temperature range. Interestingly, the activation energies associated with the hydrogen solubility of Incoloy 909 and Mo-47.5Re are very similar and approximately equal to zero. The values for the diffusivity of all the alloys lie within an order of magnitude of each other, with the diffusivity for Incoloy 909 having the smallest values.

Experimental

Hydrogen permeation for the various alloys was determined by measuring the isothermal transport of gas phase molecular hydrogen through alloy membrane specimens. Molecular hydrogen dissociatively chemisorbs on the entrance side of the membrane where it diffuses through the bulk of the membrane as protonic hydrogen [7]. The protonic hydrogen recombines on the exit side of the membrane and desorbs into the exit side volume where it is detected by a sensitive quadrupole mass analyzer. In these measurements, the exit surface volume was evacuated at a constant pumping speed so that the hydrogen partial pressure (as measured by the quadrupole mass analyzer) is directly proportional to the flux of molecules permeating the membrane. Because of its low natural abundance, deuterium was substituted for hydrogen in the Mo-47.5Re measurements to increase the sensitivity of the measurement relative to background sources of hydrogen. The apparatus was calibrated by comparing the measured signals with independently calibrated leak sources traceable to NIST standards. Other details of the apparatus and general experimental procedures are found in ref. 5 (Incoloy 909) and ref. 6 (Mo-47.5Re). The remainder of this section will describe general experimental procedures as well as those relevant to the Haynes 188 measurements.

Prior to initiating a series of measurements, the apparatus was baked at a temperature of about 200 C (390 F) for times up to 8 hours. Simultaneously, the "gauge" region of the specimen was heated to a temperature of about 700 C (1300 F) with a hydrogen pressure of 4×10^4 N/m² (300 torr) at the entrance side of the specimen. The hydrogen gas on the entrance side was purged frequently during this bake-out period. At the end of the bake-out period, the specimen was outgassed at temperature by evacuating both sides of the specimen to a high vacuum. The typical background pressure in the exit volume at the end of the bake-out period with the apparatus and the specimen at temperature was 1.3×10^{-6} N/m² (1.2×10^{-8} torr). The result of this procedure was to reduce the hydrogen background pressure (low level outgassing from the walls of the apparatus), thoroughly outgas the specimen, and produce a specimen surface which gave consistent data on a repeatable basis. The specimen was outgassed in the gauge region after each individual hydrogen charging (measurement) by heating the region to at least 700 C (1300 F) with both sides of the specimen at high vacuum.

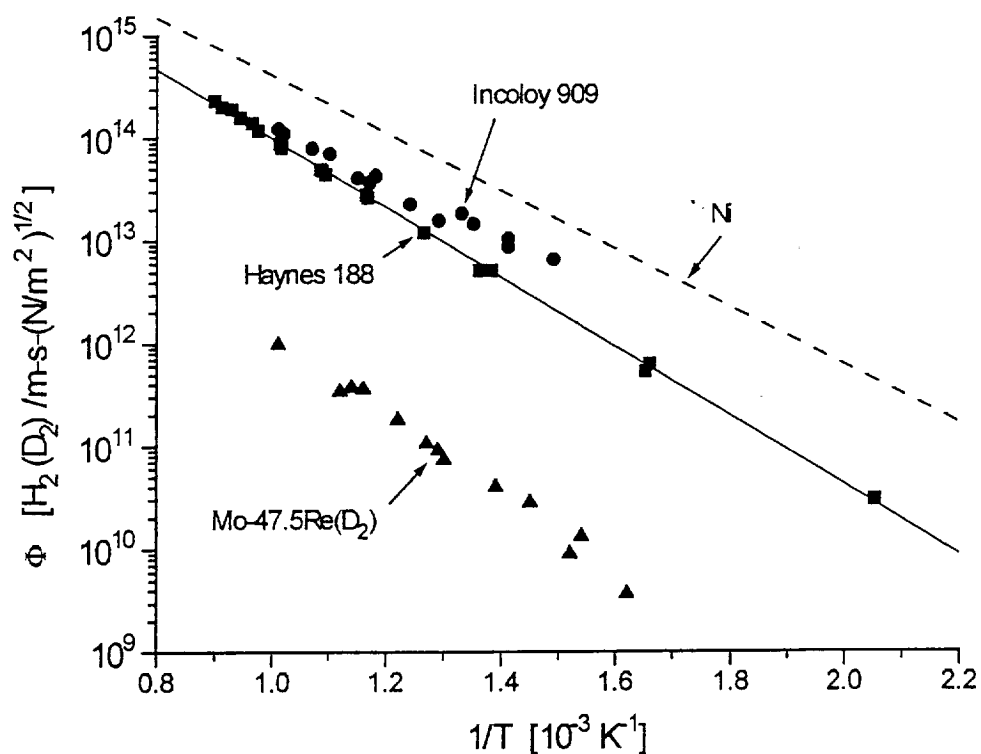


Figure 1 - Temperature dependence of the measured hydrogen (deuterium) permeability.

The Haynes 188 alloy specimen was machined from a solid rod into a closed-end cylinder. The alloy was used in the mill annealed condition. The interior specimen radius is 4.76×10^{-3} m (3/16 in.) with a wall thickness of 0.51×10^{-3} m (0.020 in.) in the gauge section. The wall thickness outside of the gauge section is 4.76×10^{-3} m (3/16 in.). The length of isothermal "hot zone" of the gauge section is 19.1×10^{-3} m (0.75 in.). The specimen in the gauge section was polished to a 600 grit surface finish. The temperature of the gauge section was measured with a thermocouple placed inside the specimen tube and contacting the interior specimen wall. The gauge section was heated by an rf induction heater located around the exterior of the gauge section. The specimen assembly (the alloy tube plus associated vacuum flanges) was thoroughly cleaned and dried before installing in the permeation apparatus, an all metal apparatus constructed from ultra high vacuum components. Data from these measurements

were analyzed using the appropriate equations for permeation through a cylindrical geometry [8].

Results

The permeation data for these alloys was obtained over a hydrogen (deuterium) pressure range of $1.3 \times 10^3 \text{ N/m}^2$ to about $1.2 \times 10^5 \text{ N/m}^2$ (10-800 torr). The temperature ranges employed for the different alloys are as follows: (1) 400 to 810 C (750-1490 F) for Incoloy 909, (2) 250 to 880 C (480-1615 F) for Haynes 188, and (3) 340 to 750 C (640-1380 F) for Mo-47.5Re. Although the data is not presented here, the permeation flux for these alloys was observed to be directly proportional to $p^{1/2}$ at several measurement temperatures [5,6]. This result suggests that the subsurface hydrogen concentration obeyed Sievert's Law and that surface reactions were not rate limiting for hydrogen permeation, i.e., permeation was rate limited by transport of hydrogen (deuterium) through the specimen bulk [7].

Permeability

The permeability, Φ , was calculated from the value of the steady-state permeation flux using the parameters and relations suitable for cylindrical geometry membranes (Incoloy 909 and Haynes 188) [5] or flat-plate membranes (Mo-47.5Re) [6]. The temperature dependence of the permeability, Φ , for the three alloys is shown as an Arrhenius plot in Fig. 1 [9]. For reference purposes, shown in Fig 1 is the permeability for pure Ni [10]. The parameters for the permeability were obtained from a least squares regression analysis, with the permeability having the form, $\Phi = \Phi_0 \times \exp (-E_\Phi/RT)$, where R is in units of kJ/mole·K and T is the temperature in Kelvin. The parameters obtained from the analysis are presented in Table II.

Table II Arrhenius Parameters from Least-Squares Fit to Permeability and Diffusivity Data

	Permeability, $\text{H}_2(\text{D}_2)/\text{m}\cdot\text{s}(\text{N/m}^2)^{1/2}$		Diffusivity, m^2/s	
	Φ_0	$E_\Phi(\text{kJ/mole})$	D_0	$E_D(\text{kJ/mole})$
Incoloy 909	5.6×10^{16}	51.1	1.2×10^{-6}	51.0
Haynes 188	2.4×10^{17}	64.6	4.8×10^{-7}	42.6
Mo-47.5Re	9.8×10^{15}	74.4	1.4×10^{-4}	74.4

Diffusivity

The diffusivity, D, was determined from the transient behavior of the permeation flux as a function of time. Values for the diffusivity for Incoloy 909 and Mo-47.5Re were determined using the appropriate formulas and the estimated "break-through time" [5,6]. The "break-through-time" is essentially the time required for the hydrogen (deuterium) to diffuse from the entrance side of the specimen to the exit side. For the Haynes 188 alloy, the diffusivity was determined from the "lag-time," where the "lag-time" was determined as the time axis intercept of the straight line, long time behavior of the time integral of the permeation flux [8]. Both procedures give identical results for the diffusivity as determined from numerical permeation simulations as well as from the analysis of actual data. The temperature dependence of the diffusivity for these alloys is presented as an Arrhenius plot in Fig. 2. Again, for references purposes, the diffusivity of pure Ni is shown [10]. The parameters for the diffusivity were obtained from a least squares regression analysis of the appropriate data set with the diffusivity having the form, $D = D_0 \times \exp (-E_D/RT)$. The parameters obtained from the analysis are presented in Table II.

Solubility

The permeability, Φ , and the diffusivity, D , were used to estimate the hydrogen (deuterium) solubility, S ; where $S = \Phi / D$ [8]. Since the permeability and diffusivity measurements were often made independent of each other, the solubility for each alloy was estimated using the results from the appropriate least-squares regression analysis. The results for the solubility of

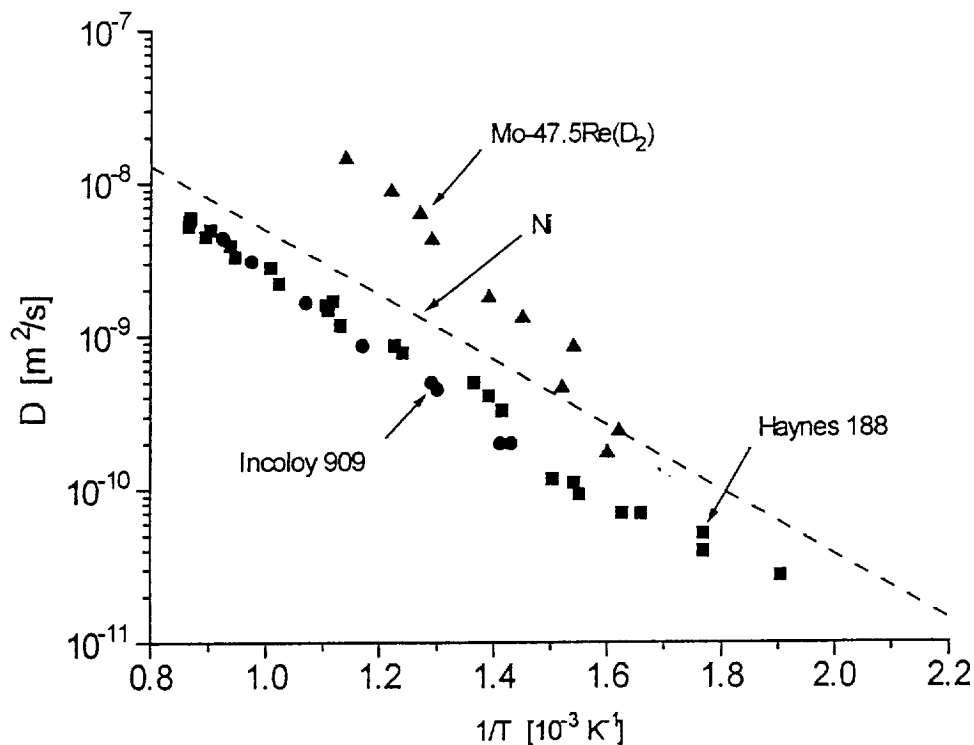


Figure 2 - Temperature dependence of the measured hydrogen (deuterium) diffusivity.

each alloy, as well as the reference metal, Ni, are shown in Fig. 3. The solubility Arrhenius parameters are not included in Table II, since they are easily calculated from the permeability and diffusivity parameters presented therein.

Discussion

The data in Figs. 1 and 2 show that the permeability and diffusivity of Incoloy 909 and Haynes 188 are similar in magnitude over a broad elevated temperature range (450 to 1500 F). In addition, they both vary less than an order of magnitude from the Ni reference data. The permeability of the Mo-47.5Re alloy is, however, significantly smaller compared with the Incoloy 909 and Haynes 188 data, while the diffusivity is noticeably higher, especially at temperatures greater than about 400 C (750 F). Based on the data, it would be expected that the high temperature transport of hydrogen within a Mo-47.5Re structure would occur more rapidly compared with a corresponding Incoloy 909 or Haynes 188 structure, but that the net flux of hydrogen through the structure under steady-state conditions will be significantly less with the Mo-47.5Re structure. Since deuterium was substituted for hydrogen in the Mo-47.5Re measurements, it is expected that the corresponding absolute values for the hydrogen permeability and diffusivity of this alloy would be about 40% larger than the deuterium values shown in Figs. 1 and 2 [11]. This correction, however, does not invalidate the scenario outlined above.

The small hydrogen permeability values for Mo-47.5Re lead to the small values for the estimated hydrogen solubility shown in Fig. 3. (It should be noted that the deuterium solubility presented Fig. 3 should be equal to the corresponding hydrogen solubility, because the isotope effect, which is present in the permeability and diffusivity transport parameters, is not present in the solubility, an equilibrium parameter [11].) The solubility for Mo-47.5Re, as shown in Fig. 3, is one to two orders of magnitude smaller than the corresponding Incoloy 909 or Haynes 188 values for temperatures above about 400 C (750 F). Since the Haynes 188 solubility has a more significant temperature dependence than Mo-47.5Re, the (extrapolated) Haynes 188 solubility will equal the Mo-47.5Re solubility at about 68 F (20 C). At lower temperatures, the Haynes 188 solubility will be less than the Mo-47.5Re solubility.

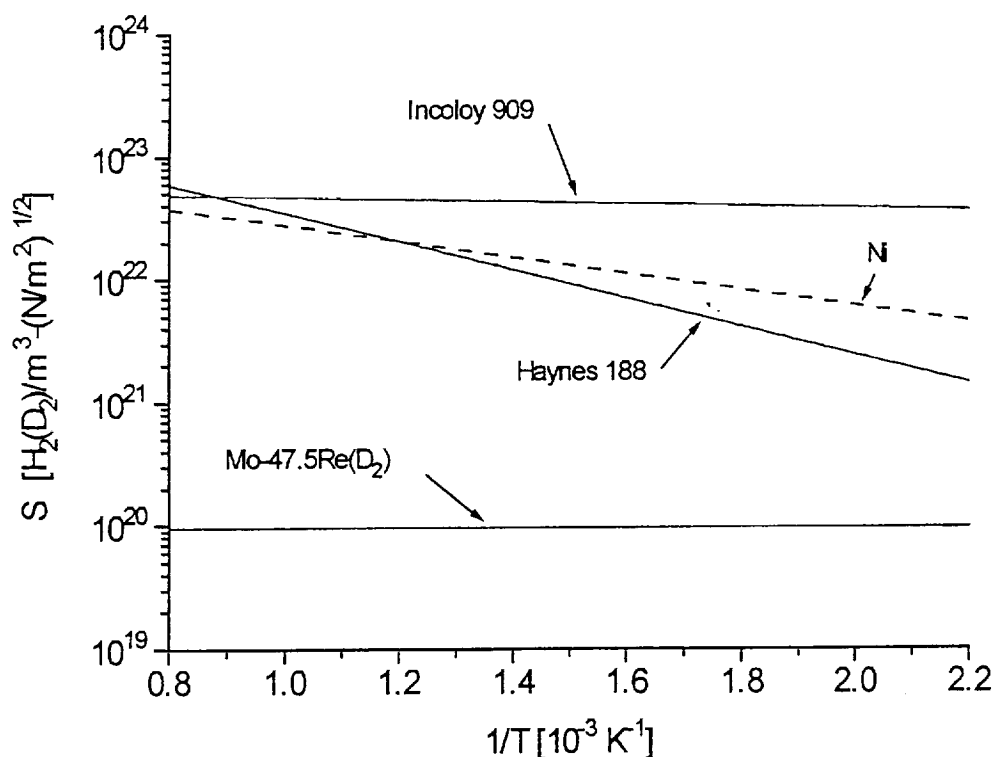


Figure 3 - Temperature dependence of the estimated hydrogen (deuterium) solubility.

The solubility values for Incoloy 909 and Mo-47.5Re shown in Fig. 3 are essentially independent of temperature. Such a weak temperature dependence in the solubility appears to be somewhat unusual. A temperature independent solubility would be desirable in those engineering applications where hydrogen charged components under go rapid temperature excursions. For example, rapid cooling would lead to super saturation of the lattice hydrogen for Haynes 188 components which had been charged to equilibrium solubility at elevated temperatures. Condensation of the supersaturated hydrogen at internal interfaces could produce a degradation of this alloy's mechanical properties, especially under conditions of rapid thermal cycling [12]. Such a situation would not occur with Incoloy 909 or Mo-47.5Re, since the solubility is essentially independent of temperature.

Conclusions

Gas phase hydrogen transport parameters for the high temperature alloys Incoloy 909, Haynes 188, and Mo-47.5Re have been measured and compared. The hydrogen permeability and diffusivity for Incoloy 909 and Haynes 188 are similar at elevated temperature (450 to 1500 F).

Over the same temperature range, the permeability for Mo-47.5Re is significantly smaller compared with the other two alloys, whereas the diffusivity is larger for temperatures above about 400 C (750 F). The hydrogen solubility for Incoloy 909 and Mo-47.5Re is essentially independent of temperature, with the solubility for Mo-47.5Re being at least two orders of magnitude smaller than the corresponding values for Incoloy 909. The solubility of Haynes 188 is temperature dependent, approaching the temperature independent value for Incoloy 909 at high temperature (820 C) and decreasing to the temperature independent value for Mo-47.5Re at about 20 C.

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